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SYNTHESIS AND STRUCTURE OF ZIRCON-BASED CERAMIC PIGMENTS CONTAINING Mn, Co, AND Ni AS CHROMOPHORIC ELEMENTS

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Zircon ceramic pigments with grey, lilac, and grey-lilac colors have been obtained using the technology developed for solid-phase sintering based on the raw materials $SiO_2 \cdot nH_2O$, ZrO_2 and MnO_2, Co_3O_4, and NiO as the source of chromophores. The sizes of the crystals range from 2 – 5 to 10 μm, respectively. The synthesized pigments are investigated by means of x-ray phase analysis using a spectral photometer and a scanning electron microscope.

Key words: pigment, zircon, color, solid-phase sintering.

Zircon ceramic pigments are used mainly because of their high-temperature stability combined with pleasant color. The basis for zircon pigment is the mineral zircon $ZrSiO_4$, which acts as an acceptor, i.e., it accepts the color ion [1]. Pure zircon is a colorless crystalline material but because of the impurities present in the crystal lattice zircon can acquire color.

The strong crystal lattice of zircon $ZrSiO_4$ is exceptionally favorable for obtaining zircon pigments. $ZrSiO_4$ synthesis from oxides without a mineralizer proceeds at temperatures above 1300°C, but at this temperature it is impossible to introduce colorant ions into the zircon lattice. For this reason, they must be synthesized at lower temperatures, which is possible if mineralizers are used — usually alkali fluorides (LiF, NaF) or silicon fluorides (Na_2SiF_6, K_2SiF_6) [2].

The role of fluorides in the synthesis of pigments is due to their lower melting temperature as compared with other components of the reaction mixture. The volatile SiF_4 obtained plays a transport role and transfers Si^{4+} ions to the location of the reaction with ZrO_2, as a result of which zircon forms.

Aside from the widely known zircon pigments with vanadium, iron, and praseodymium, experiments to obtain pigments were also performed with the participation of other elements, such as, chromium, magnesium, cobalt, copper, and others [3].

Most investigators focus attention on the mechanism of formation of zircon pigments, the role of mineralizers, and the possibility of using various raw materials in obtaining the pigments.

In recent years quite a large number of zircon pigments have been synthesized using also the sol-gel technology at considerably lower synthesis temperatures.

The main raw materials for synthesis of pigments are $SiO_2 \cdot nH_2O$ and ZrO_2. The raw material $SiO_2 \cdot nH_2O$ used for introducing SiO_2 into the mix for obtaining pigment is much more reactive than the ordinary quartz sand and is characterized by particle size dispersity 2 – 7 μm. MnO_2, Co_3O_4, and NiO were used as the raw material for introducing the chromophoric element. The amount of the chromophoric elements introduced was 5% (atomic content). K_2SiF_6 was used as the mineralizer. In this case mineralizers with a univalent alkali ion, such as Me_2SiF_6, were chosen since they form melts with lower surface tension and are much more active than mineralizers with a bivalent alkali-earth ion of the type MeX_2.

The compositions of the synthesized pigments are presented in Table 1.

The solid-phase sintering technology was used to synthesis the pigments. The samples were sintered at 800, 900, and 1000°C with isothermal soaking for 4 h at the maximum temperature.

TABLE 1. Compositions of Synthesized Pigments

Chromophore	Content, wt.%					
	ZrO_2	$SiO_2 \cdot nH_2O$	K_2SiF_6	MnO_2	Co_3O_4	NiO
5%* Mn^{2+}	53.9	34.4	5.1	6.6	–	–
5%* Co^{2+}	54.4	34.7	5.1	–	5.8	–
5%* Ni^{2+}	54.6	34.8	5.1	–	–	5.5

* Atomic content.

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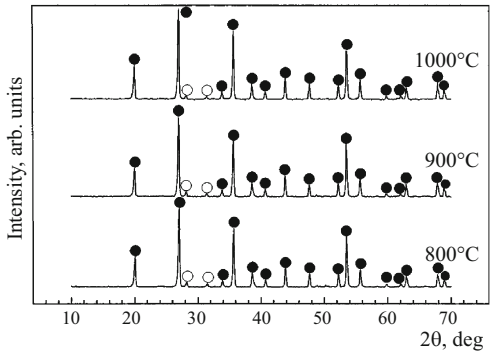

Fig. 1. X-ray diffraction pattern of the pigments with 5% Co^{2+}; mineralizer K_2SiF_6: ●) $ZrSiO_4$; ○) ZrO_2 (monoclinic).

The technological developed for synthesizing zircon pigments includes the following:

fabrication of the initial charge;

addition of a mineralizer and chromophore;

dry homogenization;

heat treatment at the indicated temperatures.

After synthesis using the scheme described, the pigments were evaluated and analyzed.

The pigments obtained after sintering were studied by x-ray phase analysis performed with a Philips APD-15 diffractometer (CuK_α radiation) to study phase formation as a function of the temperature and the type of chromophoric ion.

The color coordinates of the synthesized pigments were determined using an Elrepho-2000 spectral photometer and a D-65 light source at observation angle 10°.

The synthesized pigments were also studied with an SEM-400 Philips scanning electron microscope with acceleration voltage 80 kV. The magnifications used were varied from × 7000 to × 19,000 depending on the dimensions of the recorded microstructural elements.

When pigments with the atomic content of the chromophores Co^{2+}, Mn^{2+}, and Ni equal to 5% were used, the following was observed. For 5% Co^{2+} content the main phase $ZrSiO_4$ already appears even at 800°C as the dominant phase (Fig. 1), even though negligible reflections corresponding to interplanar distances of baddeleyite — ZrO_2 (monoclinic) are still observed. As temperature increases, the intensity of the lines of the main phase — zircon — increases due to ZrO_2. Complete synthesis of $ZrSiO_4$ is observed at 900°C, which is optimal for synthesis of these pigments.

TABLE 2. Color Coordinates of Synthesized Pigments

Pigment	*t*, °C	L^*	a^*	b^*
5%* Mn^{2+}	800	45.38	– 1.4	3.5
5%* Mn^{2+}	1000	52.47	0.9	3.8
5%* Co^{2+}	800	58.34	2.8	– 8.3
5%* Co^{2+}	1000	66.54	4.8	– 7.9
5%* Ni^{2+}	800	69.46	– 1.3	6.9
5%* Ni^{2+}	1000	77.33	– 2.1	13.2

* Atomic content.

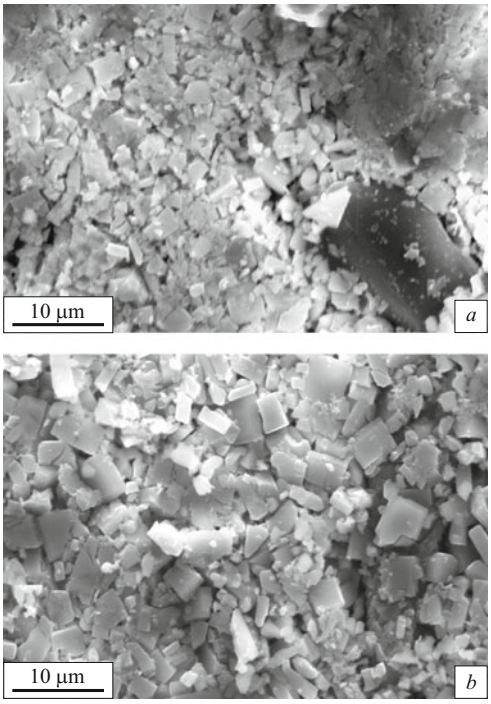

Fig. 2. Photomicrograph of pigments with 5% Mn^{2+} (atomic content), sintered at temperatures: *a*) 800°C and *b*) 1000°C.

The phase picture is similar in pigments with 5% Mn^{2+} and 5% Ni^{2+}. Large differences in the diffraction patterns are not observed with increasing temperature of synthesis. It was established that the optimal synthesis temperature of the pigments was 900°C.

The color coordinates of the pigments obtained were measured in the system CIELab (Table 2), where L^* is the brightness, $L^* = 0$ corresponds to black, $L^* = 100$ corresponds to white; a^* — green (–)/red (+); b^* — blue (–)/yellow (+).

In pigments with 5% Co^{2+} the color is lilac and grey-lilac; L^* and a^* increase with temperature.

The synthesized pigments presented in the form of powder and massive materials with different composition and thermal history were studied with an electron microscope. Depending on the type of samples, two types of preparatory techniques were used — single-step replicas for powders and two-step replicas for bulk samples.

In the bulk samples it was found that different microformations of amorphous and crystalline character were present and their dimensions were determined. In powder samples the amount and dimensions of micropores in individual particles were determined. The relation between the microstructure, composition, and conditions of synthesis of the experimental samples was established.

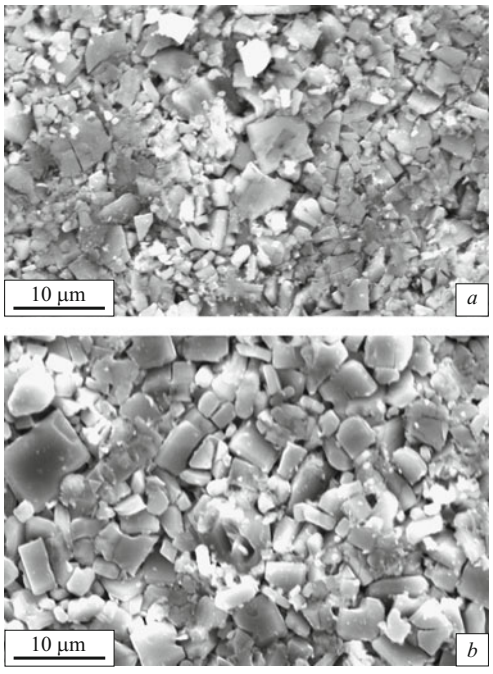

Fig. 3. Photomicrographs of pigments with 5 at.% Co^{2+}, sintered at temperatures: *a*) 800°C and *b*) 1000°C.

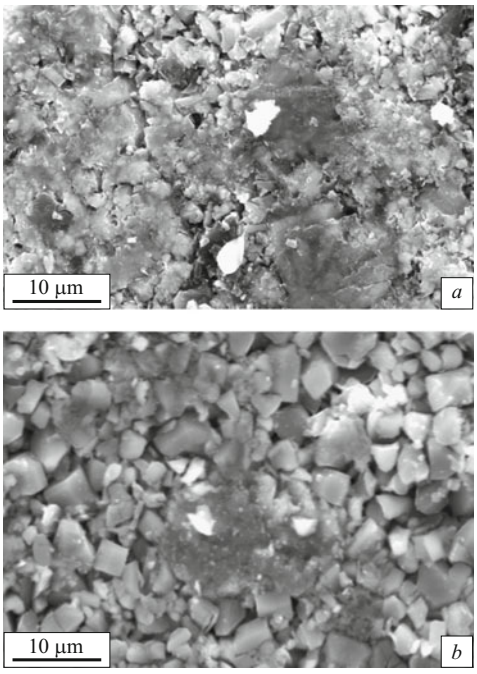

Fig. 4. Photomicrographs of pigments with 5 at.% Ni^{2+}, sintered at temperatures: *a*) 800°C and *b*) 1000°C.

Figure 2 displays photomicrographs of the pigments with 5% Mn^{2+}, sintered at different temperatures. A polydisperse structure in which Mn is distributed in 1 – 5 μm crystals is observed in pigment obtained as a result of sintering at 800°C.

As temperature increases, at 1000°C, the sample becomes monodisperse, and 1 – 2 μm single-crystals and their aggregates are present. A homogeneous distribution of manganese in the pigment is also observed.

Figure 3 shows photomicrographs of pigments with 5% Co^{2+} for different sintering temperatures. It is evident that a monodisperse structure with 2 – 5 μm crystals and uniform Co particle distribution is observed in pigment obtained by sintering at 800°C. The crystalline habitus is clearly seen.

No large changes are observed as the pigment sintering temperature increases to 1000°C.

Figure 4 shows photomicrographs of pigments with 5 at.% Ni^{2+}. It is evident that a polydisperse structure with unclear crystal forms and crystals from 2 – 5 to 10 μm is observed in pigment obtained as a result of sintering at 800°C. It is supposed that the chromophoric element Ni is concentrated in large crystals.

CONCLUSIONS

The possibility of obtaining zircon pigments using Mn, Co, and Ni as chromophoric elements is confirmed. The main phase $ZrSiO_4$ appears already at 800°C, and it is finally synthesized at 900°C. This temperature is optimal for synthesis of pigments. Pigments are characterized by the presence of crystals generally ranging in size from 2 to 5 μm. The pigments obtained can be used in glazes for ceramic articles.

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